

# PATENT ABSTRACTS OF JAPAN

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(54) PHASE DIFFERENCE FILM, ITS PRODUCTION AND LIQUID CRYSTAL DISPLAY DEVICE

(57)Abstract:

PURPOSE: To obtain such a phase difference film that the rate of temp. change can be easily adapted according to the rate of temp. change of a liquid crystal display cell to be used with combination of the film, and to obtain the production method of the phase difference film which does not require heat treatment at high temp., and to obtain a liquid crystal display device using this phase difference film having excellent display characteristics at high temp.

CONSTITUTION: This phase difference film contains a polymerized material of liquid crystal oligomer having positive intrinsic double refraction and glass transition temp. <50°C and showing a nematic or smectic phase. The optical axis of the film is in the film plane. The retardation as the product of the anisotropy of refractive index  $\Delta n$  and film thickness d of the film is >100nm at 30°C. The ratio of the retardation at 80°C to the retardation at 30°C is 0.95 to 0.5.

## JP 8-5839

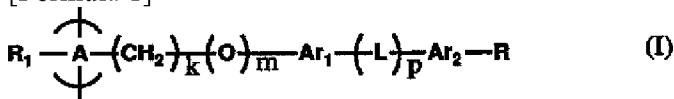
### CLAIMS

[Claim(s)]

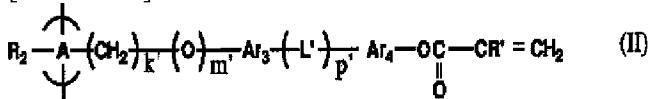
[Claim 1] It is a film containing polymer of a liquid crystal oligomer which has a positive peculiar double reflex and shows a nematic phase or a smectic phase whose glass transition temperature is 50 \*\* or less, An optical axis of this film is in a film plane, and a value at 30 \*\* of a retardation which are refractive-index-anisotropy deltan of this film and a product of the thickness d is not less than 100 nm, And a phase difference film, wherein ratios of a value at 80 \*\* to a value at 30 \*\* of a retardation are 0.95-0.5.

[Claim 2] When a liquid crystal oligomer is chosen from a straight chain or an annular liquid crystal oligomer which makes following repeating unit (I) and (II) a main constitutional unit and makes repeating unit (I) in this one molecule of oligomer, and the number of (II)s n and n', respectively, The phase difference film according to claim 1 which n and n' is an integer of 1-20 independently, respectively, it is  $4 \leq n+n' \leq 21$ , and ratios of n:n' are 20:1-1:3, and is characterized by an end group of repeating unit (II) having polymerized.

[Formula 1]

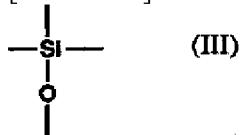


[Formula 2]

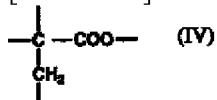


[A is a basis expressed with lower type (III) or (IV) among a formula, and in formula (III), -Si-O- is a main chain of formula (I) or (II), and in formula (IV), -C-CH<sub>2</sub>- is a main chain of formula (I) or (II), and combines a COO group with a group (CH<sub>2</sub>). When A is formula (III) in formula (I), and when A is formula (III) in formula (II), R<sub>1</sub> and R<sub>2</sub> are the alkyl groups or phenyl groups of hydrogen and the carbon numbers 1-6 independently, respectively. When A is formula (IV) in formula (I), and when A is formula (IV) in formula (II), R<sub>1</sub> and R<sub>2</sub> are hydrogen or an alkyl group of the carbon numbers 1-6 independently, respectively.

[Formula 3]



[Formula 4]



k and k' expresses the integer of 2-10 independently, respectively, and m and m' is 0 or 1 independently, respectively, Independently Ar<sub>1</sub>, Ar<sub>2</sub>, Ar<sub>3</sub>, and Ar<sub>4</sub>, respectively A 1,4-phenylene group, they are a 1,4-cyclohexane group, a pyridine- 2,5-diyl group or the pyrimidine 2, and 5-diyl group -- L and L' -- respectively -- independent -CH<sub>2</sub>-O-, -O-CH<sub>2</sub>-, and - COO-, -OCO-, -CH<sub>2</sub>-CH<sub>2</sub>-, -CH=N-, and -N=CH- or [Formula 5]



It comes out, and it is a divalent basis shown and R' is [ p and p' is 0 or 1 independently, respectively, R is halogen, a cyano group, an alkyl group of the carbon numbers 1-10, or an alkoxy group of the carbon numbers 1-10, and ] hydrogen or an alkyl group of the carbon numbers 1-5. ]

[Claim 3]The phase difference film according to claim 1 characterized by coming to form membranes on a substrate in which a phase difference film is transparent or translucent.

[Claim 4]The phase difference film according to claim 2 characterized by coming to form membranes on a substrate in which a phase difference film is transparent or translucent.

[Claim 5]The phase difference film according to claim 3 or 4 being a phase difference film which a substrate has an optical axis in a film plane, and has a positive peculiar double reflex, which consists of thermoplastic polymers, and which carried out uniaxial orientation.

[Claim 6]A manufacturing method of the phase difference film according to claim 1, 2, 3, or 4 performing heat treatment after forming the liquid crystal oligomer according to claim 2 on the substrate according to claim 3 or 4 which has an orientation means on the surface, making an optical axis be in a film plane, and polymerizing an end group of repeating unit (II) [Claim 7]After forming the liquid crystal oligomer according to claim 2 on a substrate which has an orientation means on the surface, A manufacturing method of the phase difference film according to claim 1, 2, 3, or 4 exfoliating from a substrate which has an orientation means on the surface, and transferring to the substrate according to claim 3 or 4 after heat-treating, making an optical axis be in a film plane and polymerizing an end group of repeating unit (II).

[Claim 8]A phase difference film in which it pastes together or laminates and a phase difference film which consists of a thermoplastic polymer which has an optical axis a phase difference film Claims 1, 2 and 3 or given in four and in a film plane, and has a positive peculiar double reflex, and which carried out uniaxial orientation becomes.

[Claim 9]A liquid crystal cell which consists of a liquid crystal layer which was pinched by substrate which has an electrode, and which has positive permittivity anisotropy, and twisted for it and carried out orientation of the screw axis to a substrate perpendicularly almost horizontally at the time of impressing no voltage, A liquid crystal display using at least one chosen from the phase difference film according to claim 1, 2, 3, 4, 5, or 8 arranged between a polarization film arranged at the outside, and this liquid crystal cell and this polarization film.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the liquid crystal display using the phase difference film used for a super twist nematic (it may be hereafter called STN.) mold liquid crystal display element etc., its manufacturing method, and this phase difference film.

[0002]

[Description of the Prior Art]As a light and thin planar display, the liquid crystal display is used for the indicator of a personal computer or a various device. The field used with a distribution cost is also expanded with improvement in the characteristic. The environment used also spreads in connection with it, and to operate at an elevated temperature or low temperature is demanded. As a liquid crystal display, the STN type thing is widely used for the display of a word processor or a personal computer. In the present STN type liquid crystal display, the birefringence of a liquid crystal layer is compensated with a phase difference film (generally called color compensation), and what realized black and white or a colored presentation is used. Although using the liquid crystal layer for compensation for phase

contrast compensation was performed in early stages, the high polymer film which carried out uniaxial orientation is generally used now. However, there is expansion of the use field also by a STN type liquid crystal display element, and the environment which uses an element has spread. The request of improvement of the new characteristic has come out in connection with it. One of them is that change of the quality of a display to a temperature change is small. For example, by a car, a temperature in the car changes with seasons a lot. In this case, there was a problem to which each retardations (optical phase contrast) of a liquid crystal cell and a phase difference film differ at an elevated temperature or low temperature, and display properties worsen.

[0003]That is, if temperature becomes high, a retardation will become small with relaxation of the orientation of a liquid crystal element or Polymer Division, but generally the orientation relaxation of the low-molecular liquid crystal currently used for the liquid crystal cell is larger, and change of a retardation also has it. [ larger than orientation relaxation of Polymer Division currently used for the phase difference film ] For this reason, both retardation currently optimized at the room temperature shifts from an optimal condition at an elevated temperature, color compensation of a liquid crystal cell becomes imperfect, problems, like coloring arises arise, and display properties fall. Thus, the phase difference film using a high polymer film was not necessarily ideal for characteristic improvement of a liquid crystal cell, when removing the viewpoint of color compensation. For this reason, the trial which uses a liquid crystal material for a phase difference film is also reported.

[0004]The solution which dissolved liquid crystallinity Polymer Division which becomes JP,H3-291601,A from the polyester which includes an orthosubstitution aromatic unit substantially is applied on the substrate which has a publicly known orienting film, As for more than the glass transition temperature of liquid crystallinity Polymer Division, by heat-treating below with liquid crystal phase-isotropic phase transition temperature, carry out level orientation, it is made to cool below to glass transition temperature, and what fixed orientation is illustrated. In this, the liquid crystallinity polymer material beyond the temperature which glass transition temperature uses is illustrated. The side chain type liquid crystal polymer and elastomer which have a straight chain or an annular main chain are used for JP,H4-500284,A, After extending a film above the glass transition temperature over 50 \*\*, or impressing a magnetic field and an electric field above a glass transition point and carrying out orientation of the meso gene group, it is indicated that fix orientation below with glass transition temperature, and a phase difference film is obtained. The siloxane chain which has glass transition temperature in the temperature region desirable in WO 92/No. 14180 gazette and higher than the maximum of service temperature beyond a room temperature in it, Uniaxial orientation of the liquid crystal polymer which makes a skeleton an acrylic chain or a meta-acrylic chain is heated and carried out, and the optically anisotropic body obtained by the method of quenching is indicated.

[0005]However, orientation of the meso gene group of a polymer liquid crystal needed to be carried out under heating, it needed to be cooled below to glass transition temperature, and orientation needed to be made to fix in the phase difference film using the Polymer Division liquid crystal material indicated until now. The polymer material which has a glass transition temperature higher than service temperature needed to be used. Since the glass transition point is higher than a room temperature, in order to carry out orientation of the optical axis of a liquid crystal polymer into a field, an elevated temperature needs to be heat-treated. In the temperature range to be used, since a polymer liquid crystal is a vitreous state, it has a problem to which the temperature dependence of a double refraction factor does not often necessarily follow in footsteps of the temperature change of the retardation of a liquid crystal cell unlike a liquid crystal cell. It had a fault, such as it being difficult to obtain material with a low glass transition temperature, for example, phase difference films with a mechanical strength enough in a liquid crystal oligomer, on the other hand, and it being difficult to deal

with it industrially, and being. Thus, the phase difference film in which near temperature dependence is shown by the temperature dependence of the retardation of the liquid crystal cell for a display was called for.

[0006]

[Problem(s) to be Solved by the Invention]The phase difference film to which temperature change rates can be easily fitted according to the temperature change rates of the liquid crystal display cell which the purpose of this invention uses in combination, Providing the liquid crystal display which was excellent in the display properties in the elevated temperature using the manufacturing method of this unnecessary phase difference film and this phase difference film has heat treatment in an elevated temperature.

[0007]

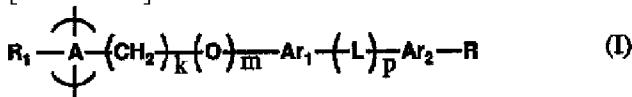
[Means for Solving the Problem]This invention persons have a positive peculiar double reflex, as a result of inquiring wholeheartedly, in order to solve the above-mentioned problem, After carrying out homogeneous orientation (level orientation) of the liquid crystal oligomer which shows a nematic phase or a smectic phase, and has a meso gene group of polymerization nature in intramolecular, a meso gene group by polymerizing, Even if a phase difference film which has an optical axis in a film plane could be obtained on a substrate or a high polymer film and it used it at an elevated temperature, it finds out that a liquid crystal display excellent in monochrome level is obtained, and came to complete this invention.

[0008]That is, this invention consists of an invention described below.

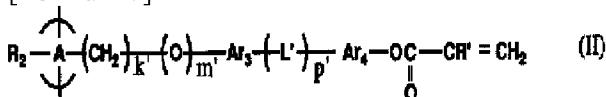
(1) It is a film containing polymer of a liquid crystal oligomer which has a positive peculiar double reflex and shows a nematic phase or a smectic phase whose glass transition temperature is 50 \*\* or less, An optical axis of this film is in a film plane, and a value at 30 \*\* of a retardation which are refractive-index-anisotropy deltan of this film and a product of the thickness d is not less than 100 nm, And a phase difference film, wherein ratios of a value at 80 \*\* to a value at 30 \*\* of a retardation are 0.95-0.5.

[0009](2) A liquid crystal oligomer is chosen from a straight chain or an annular liquid crystal oligomer which makes following repeating unit (I) and (II) a main constitutional unit, When making repeating unit (I) in this one molecule of oligomer, and the number of (II)s into n and n', respectively, n -- and -- n -- ' -- respectively -- independent -- one - 20 -- an integer -- it is - - four -- <= -- n+n -- ' -- <= -- 21 -- it is -- n:n -- ' -- a ratio -- 20:1 - 1:3 -- it is -- a repeating unit -- (II) -- an end group -- polymerizing -- \*\*\*\* -- things -- the feature -- carrying out -- (one --) -- a description -- a phase difference film .

[Formula 6]

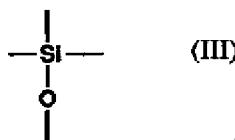


[Formula 7]

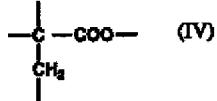


[A is a basis expressed with lower type (III) or (IV) among a formula, and in formula (III), - Si-O- is a main chain of formula (I) or (II), and in formula (IV), -C-CH<sub>2</sub>- is a main chain of formula (I) or (II), and combines a COO group with a group (CH<sub>2</sub>). When A is formula (III) in formula (I), and when A is formula (III) in formula (II), R<sub>1</sub> and R<sub>2</sub> are the alkyl groups or phenyl groups of hydrogen and the carbon numbers 1-6 independently, respectively. When A is formula (IV) in formula (I), and when A is formula (IV) in formula (II), R<sub>1</sub> and R<sub>2</sub> are hydrogen or an alkyl group of the carbon numbers 1-6 independently, respectively.

[Formula 8]



[Formula 9]



k and k' expresses the integer of 2-10 independently, respectively, and m and m' is 0 or 1 independently, respectively, Independently Ar<sub>1</sub>, Ar<sub>2</sub>, Ar<sub>3</sub>, and Ar<sub>4</sub>, respectively A 1,4-phenylene group, they are a 1,4-cyclohexane group, a pyridine- 2,5-diyl group or the pyrimidine 2, and 5-diyl group -- L and L' -- respectively -- independent -CH<sub>2</sub>-O-, -O-CH<sub>2</sub>-, and - COO-, -OCO-, -CH<sub>2</sub>-CH<sub>2</sub>-, -CH=N-, and -N=CH- or [Formula 10]



It comes out, and it is a divalent basis shown and R' is [ p and p' is 0 or 1 independently, respectively, R is halogen, a cyano group, an alkyl group of the carbon numbers 1-10, or an alkoxy group of the carbon numbers 1-10 and ] hydrogen or an alkyl group of the carbon numbers 1-5. ]

[0010](3) Phase difference film given in (1) characterized by coming to form membranes on a substrate in which a phase difference film is transparent or translucent.

[0011](4) Phase difference film given in (2) characterized by coming to form membranes on a substrate in which a phase difference film is transparent or translucent.

[0012](5) A phase difference film (3) or given in (4) being a phase difference film which a substrate has an optical axis in a film plane, and has a positive peculiar double reflex, which consists of thermoplastic polymers, and which carried out uniaxial orientation.

[0013](6) After forming a liquid crystal oligomer of the aforementioned (2) description on a substrate (3) which has an orientation means on the surface, or given in (4), A manufacturing method of a phase difference film (1), (2), (3), or given in (4) heat-treating, making an optical axis be in a film plane, and polymerizing an end group of repeating unit (II) [0014](7) After forming a liquid crystal oligomer of the aforementioned (2) description on a substrate which has an orientation means on the surface, A manufacturing method of a phase difference film (1), (2), (3), or given in (4) exfoliating from a substrate which has an orientation means on the surface, and transferring to a substrate (3) or given in (4) after heat-treating, making an optical axis be in a film plane and polymerizing an end group of repeating unit (II).

[0015](8) A phase difference film in which it pastes together or laminates and a phase difference film which consists of a thermoplastic polymer which has an optical axis a phase difference film the above (1), (2), (3), or given in (4) and in a film plane, and has a positive peculiar double reflex, and which carried out uniaxial orientation becomes.

[0016](9) A liquid crystal cell which consists of a liquid crystal layer which was pinched by substrate which has an electrode, and which has positive permittivity anisotropy, and twisted for it and carried out orientation of the screw axis to a substrate perpendicularly almost horizontally at the time of impressing no voltage, A liquid crystal display using at least one chosen from a phase difference film (1), (2), (3), (4), (5), or given in (8) arranged between a polarization film arranged at the outside, and this liquid crystal cell and this polarization film.

[0017]Next, this invention is explained in detail. Glass transition temperature is 50 \*\* or less, and a phase difference film of this invention is a film containing liquid crystal oligomer polymer which has polymerized at the end of a meso gene group which constitutes it in a liquid crystal oligomer which shows a nematic phase or a smectic phase. If it has a meso gene

group of polymerization nature as these liquid crystal oligomers. Although there is no restriction in particular, a side chain type liquid crystal oligomer which is a liquid crystal oligomer which has a polymerization nature group which consists of repeating unit (I) and (II), and has a positive peculiar double reflex by a liquid crystal state, and takes a nematic phase or a smectic phase is preferred. Although Polly 1-alkyl acrylic ester, a polysiloxane, etc. are illustrated as a skeleton chain of a side chain type liquid crystal oligomer and a straight chain or an annular thing can be used, an annular structure is preferred from a viewpoint of the chemical stability of a liquid crystal oligomer. In Polly 1-alkyl acrylic ester, polymethacrylic acid ester or polyacrylic ester is polymethacrylic acid ester desirable still more preferably. In these, a side chain type liquid crystal oligomer of a polysiloxane system is preferred. What was combined with a main chain can generally use a basis (it may be hereafter called a meso gene group.) which gives liquid crystallinity via a crookedness chain (it may be hereafter called a spacer.).

[0018]Although there is no restriction in particular about temperature of a maximum which shows a liquid crystal state of a polymerization nature liquid crystal oligomer, for desiccation at the time of lamination with a substrate, or orientation treatment, So that transition temperature (it may be hereafter described as transition temperature of a liquid crystal phase/isotropic phase.) from a liquid crystal phase to an isotropic phase may be 200 \*\* or less preferably, It is desirable to choose the length of a spacer, a kind of meso gene group, and the number of repeating units so that it may become 150 \*\* or less preferably especially so that it may become 170 \*\* or less still more preferably. About transition temperature (it may be hereafter described as a glass transition point.) of a crystal phase or a glass phase, and a liquid crystal phase, the lower one is preferred from conformity with the temperature dependence of a double reflex of a liquid crystal cell, and 50 \*\* or less is specifically 30 \*\* or less desirable still more preferably.

[0019]Several n and n' of a repeating unit of a polymerization nature liquid crystal oligomer which are used by this invention are the integers from 1 to 20 independently, and they are chosen, respectively so that the sum total of n and n' may be set to 21 from 4. From a viewpoint of immobilization of the stacking tendency of a liquid crystal oligomer, and orientation after a polymerization, a range of a ratio of n and n' is 20:1 to 1:3, and it is 3:1 to 1:2 preferably [ it is desirable and ] to 3:1 to 1:3, and a pan. Control of a ratio of n and n' can be performed when compounding these liquid crystal oligomers like the after-mentioned.

[0020]Also by a spacer with which this liquid crystal oligomer connects a meso gene group to a main chain, liquid crystal transition temperature and a stacking tendency are influenced. In a short spacer, since relaxation after orientation of a meso gene group takes place easily in a spacer with the stacking tendency of a meso gene group long not good, an alkylene group or an alkyleneoxy group to the carbon numbers 2-10 is preferred as a spacer. An alkylene group or an alkyleneoxy group from a viewpoint of the tropism of your kind consideration to the carbon numbers 2-6 is especially preferred. A composite ease to an alkyleneoxy group is more preferred. As a desirable basis, concretely -(CH<sub>2</sub>)<sub>2</sub>-, -(CH<sub>2</sub>)<sub>3</sub>-, -(CH<sub>2</sub>)<sub>4</sub>-, -(CH<sub>2</sub>)<sub>5</sub>-, -(CH<sub>2</sub>)<sub>6</sub>-, -(CH<sub>2</sub>)<sub>3</sub>-O-, -(CH<sub>2</sub>)<sub>4</sub>-O-, -(CH<sub>2</sub>)<sub>5</sub>-O-, and -(CH<sub>2</sub>)<sub>6</sub>-O- are illustrated.

[0021]In a phase difference film containing liquid crystal oligomer polymer in which this invention carried out orientation, it is advantageous on industry that the anisotropy of a refractive index is large. For the purpose, a refractive index anisotropy big basis of a meso gene group is preferred. As a structure of giving such a meso gene group, A thing of a 1,4-phenylene group, a 1,4-cyclohexane group, a pyridine- 2,5-diyl group, or a pyrimidine 2,5-diyl group is independently mentioned for Ar<sub>1</sub> in repeating unit (I) or a (II) type, Ar<sub>2</sub>, Ar<sub>3</sub>, and Ar<sub>4</sub>, respectively. the divalent basis L which combines Ar<sub>1</sub>, Ar<sub>2</sub>, or Ar<sub>3</sub> and Ar<sub>4</sub> -CH<sub>2</sub>-O-, -O-CH<sub>2</sub>-, and -COO-, -OCO-, -CH<sub>2</sub>-CH<sub>2</sub>-, -CH=N-, and -N=CH- or [0022]

[Formula 11]



It comes out and the divalent basis shown is mentioned. The basis which the basis (when it is p=0) or Ar<sub>3</sub> which Ar<sub>1</sub> and Ar<sub>2</sub> coupled directly, and Ar<sub>4</sub> coupled directly is mentioned (when it is p'=0). In these, preferably, Ar<sub>1</sub>, Ar<sub>2</sub>, Ar<sub>3</sub>, and Ar<sub>4</sub> are a 1,4-phenylene group, a pyridine-2,5-diyl group, and a pyrimidine 2,5-diyl group independently, respectively, and are a 1,4-phenylene group still more preferably. -CH<sub>2</sub>-CH<sub>2</sub>-, -COO-, and a -OCO-basis are desirable still more preferred independently, and the bond groups L and L' are -COO-bases, respectively.

[0023] Since the R group in repeating unit (I) influences the permittivity anisotropy and the stacking tendency of a meso gene group, halogen, a cyano group, the alkyl group of the carbon numbers 1-10, or the alkoxy group of the carbon numbers 1-10 is chosen from a viewpoint of obtaining a refractive index anisotropy high liquid crystal oligomer film.

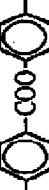
Preferably, it is a cyano group, an alkyl group of the carbon numbers 1-10, or an alkoxy group of the carbon numbers 1-10, and they are a cyano group or an alkoxy group of the carbon numbers 1-10 still more preferably.

[0024] An end group in repeating unit (II) is a basis for fixing orientation of a liquid crystal oligomer by polymerization. As a polymerization group - It is OCO-C(R') =CH<sub>2</sub> (R' expresses hydrogen or an alkyl group of the carbon numbers 1-5.), and an acrylate group and a methacrylate group are illustrated. Although there is no restriction in particular in a polymerization method of these bases, photopolymerization and thermal polymerization by a radical initiator are illustrated, and a viewpoint of simplicity of operation or efficiency of immobilization of orientation to photopolymerization is preferred. A thing publicly known as an initiator of photopolymerization can be used.

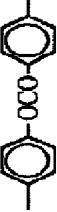
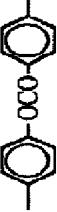
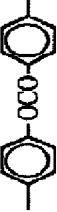
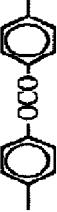
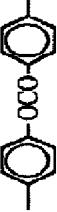
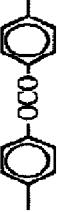
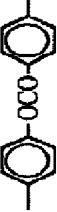
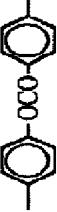
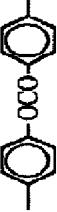
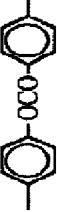
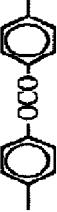
[0025] A non-polymerizable meso gene group used for straight chain shape or an annular liquid crystal oligomer with a repeating unit shown in repeating unit (I) is illustrated below. For example, in Table 1, Ar<sub>1</sub>-(L)<sub>p</sub>-Ar<sub>2</sub> is a diphenyl group, and the number 1 shows a non-polymerizable meso gene group which R group is a -CN basis and is a -(CH<sub>2</sub>)<sub>3</sub>-basis as a spacer. The following is also the same meaning.

[0026]

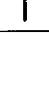
[Table 1]

$A_1(L)_p-A_2$	R <sub>基</sub>	$\lambda^{\wedge} \leftarrow \# -$					
		$-(CH_2)_3-$	$-(CH_2)_4-$	$-(CH_2)_5-$	$-(CH_2)_3-0-$	$-(CH_2)_4-0-$	$-(CH_2)_5-0-$
 同上	-CN	1	2	3	4	6	6
	-OCH <sub>3</sub>	7	8	9	10	11	12
	-OC <sub>2</sub> H <sub>5</sub>	1.3	1.4	1.5	1.6	1.7	1.8
	-C <sub>6</sub> H <sub>13</sub>	1.9	2.0	2.1	2.2	2.3	2.4
	-F	2.5	2.6	2.7	2.8	2.9	3.0
 同上	-CN	3.1	3.2	3.3	3.4	3.5	3.6
	-OCH <sub>3</sub>	3.7	3.8	3.9	4.0	4.1	4.2
	-OC <sub>2</sub> H <sub>5</sub>	4.3	4.4	4.5	4.6	4.7	4.8
	-C <sub>6</sub> H <sub>13</sub>	4.9	5.0	5.1	5.2	5.3	5.4
	-F	5.5	5.6	5.7	5.8	5.9	6.0

[0027]  
 [Table 2]

$A_{I_1}^{\bullet}(L) - A_{I_2}^{\bullet}$	R <sub>基</sub>	λペーパー					
		-(CH <sub>2</sub> ) <sub>3</sub> -	-(CH <sub>2</sub> ) <sub>4</sub> -	-(CH <sub>2</sub> ) <sub>5</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> -O-	-(CH <sub>2</sub> ) <sub>4</sub> -O-	-(CH <sub>2</sub> ) <sub>5</sub> -O-
	-CN	6.1	6.2	6.3	6.4	6.5	6.6
	-OCH <sub>3</sub>	6.7	6.8	6.9	7.0	7.1	7.2
	-OC <sub>2</sub> H <sub>5</sub>	7.3	7.4	7.5	7.6	7.7	7.8
	-C <sub>6</sub> H <sub>13</sub>	7.9	8.0	8.1	8.2	8.3	8.4
	-F	8.5	8.6	8.7	8.8	8.9	9.0
  	-CN	9.1	9.2	9.3	9.4	9.5	9.6
	-OCH <sub>3</sub>	9.7	9.8	9.9	1.00	1.01	1.02
	-OC <sub>2</sub> H <sub>5</sub>	1.03	1.04	1.05	1.06	1.07	1.08
	-C <sub>6</sub> H <sub>13</sub>	1.09	1.10	1.11	1.12	1.13	1.14
	-F	1.15	1.16	1.17	1.18	1.19	1.20

[0028]  
[Table 3]

$\text{Ar}_1\text{-}(\text{I})_p\text{-}\text{Ar}_2$	R $\ddagger$	$\lambda^{\alpha-\beta-}$				
		$-(\text{CH}_2)_3^-$	$-(\text{CH}_2)_4^-$	$-(\text{CH}_2)_5^-$	$-(\text{CH}_2)_3^-0^-$	$-(\text{CH}_2)_4^-0^-$
	-CN	1.21	1.22	1.23	1.24	1.25
同 上	-OCH <sub>3</sub>	1.27	1.28	1.29	1.30	1.31
同 上	-OC <sub>2</sub> H <sub>5</sub>	1.33	1.34	1.35	1.36	1.37
同 上	-C <sub>6</sub> H <sub>13</sub>	1.39	1.40	1.41	1.42	1.43
同 上	-F	1.45	1.46	1.47	1.48	1.49
$\lambda^{\alpha-\beta-}$		1.51	1.52	1.53	1.54	1.55
	-OCH <sub>3</sub>	1.57	1.58	1.59	1.60	1.61
同 上	-OC <sub>2</sub> H <sub>5</sub>	1.63	1.64	1.65	1.66	1.67
同 上	-C <sub>6</sub> H <sub>13</sub>	1.69	1.70	1.71	1.72	1.73
同 上	-F	1.75	1.76	1.77	1.78	1.79
$\lambda^{\alpha-\beta-}$		1.80	1.80	1.80	1.80	1.80

[0029]  
 [Table 4]

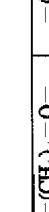
$\text{Ar}_1^*(\text{L})_p \cdot \text{Ar}_2$	R <sup>‡</sup>	λ<math>\lambda</math>-<math>\eta</math>-				
		- $(\text{CH}_2)_3-$	- $(\text{CH}_2)_4-$	- $(\text{CH}_2)_5-$	- $(\text{CH}_2)_3-\text{O}-$	- $(\text{CH}_2)_4-\text{O}-$
	-CN	181	182	183	184	185
同上	-OCH <sub>3</sub>	187	188	189	190	191
同上	-OC <sub>2</sub> H <sub>5</sub>	193	194	195	196	197
同上	-C <sub>6</sub> H <sub>13</sub>	199	200	201	202	203
同上	-F	205	206	207	208	209
	-CN	211	212	213	214	215
同上	-OCH <sub>3</sub>	217	218	219	220	221
同上	-OC <sub>2</sub> H <sub>5</sub>	223	224	225	226	227
同上	-C <sub>6</sub> H <sub>13</sub>	229	230	231	232	233
同上	-F	235	236	237	238	239

[0030]The bases of the numbers 1-6, 31-36, 61-66, 181-186, 211-216 which have a cyano group in these meso gene groups are the numbers 31-36 desirable still more preferably. These meso gene groups are preferred from a stacking tendency with what [ high ] was combined with the polysiloxane system main chain being shown, and especially their thing combined with cyclosiloxane is preferred.

[0031]The meso gene group of polymerization nature used for straight chain shape or an annular liquid crystal oligomer with repeating unit (II) is illustrated below.

[0032]

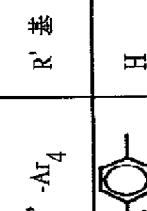
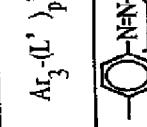
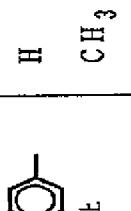
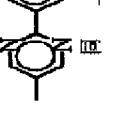
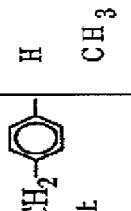
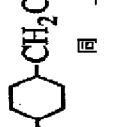
[Table 5]

$\text{Ar}_3^*-(\text{L}')_p^*-\text{Ar}_4^*$	$\text{R}'$	$-\text{(CH}_2)_3-$	$-\text{(CH}_2)_4-$	$-\text{(CH}_2)_5-$	$-\text{(CH}_2)_3-\text{O}-$	$-\text{(CH}_2)_4-\text{O}-$	$-\text{(CH}_2)_5-\text{O}-$
	H	241	242	243	244	245	246
	CH <sub>3</sub>	247	248	249	250	251	252
	H	253	254	255	256	257	258
	CH <sub>3</sub>	259	260	261	262	263	264

[0033]  
 [Table 6]

$\text{Ar}_3^{\cdot}(\text{L}')_p^{\cdot} \text{Ar}_4^{\cdot}$	$\text{R}'$	$\text{基}$	$-(\text{CH}_2)_3-$	$-(\text{CH}_2)_4-$	$-(\text{CH}_2)_5-$	$-(\text{CH}_2)_3-\text{O}-$	$-(\text{CH}_2)_4-\text{O}-$	$-(\text{CH}_2)_5-\text{O}-$
 同上	H		265	266	267	268	269	270
	$\text{CH}_3$		271	272	273	274	275	276
 同上	H		277	278	279	280	281	282
	$\text{CH}_3$		283	284	285	286	287	288
 同上	H		289	290	291	292	293	294
	$\text{CH}_3$		295	296	297	298	299	300

[0034]  
 [Table 7]

$\text{Ar}_3^-(\text{L}')_p^+ \cdot \text{Ar}_4$	$\text{R}'^{\#}$	$\lambda \wedge -\ddagger-$
	H	- $(\text{CH}_2)_3^-$
	$\text{CH}_3$	- $(\text{CH}_2)_4^-$
	H	- $(\text{CH}_2)_5^-$
	$\text{CH}_3$	- $(\text{CH}_2)_3^-$
	H	- $(\text{CH}_2)_4^-$
	$\text{CH}_3$	- $(\text{CH}_2)_5^-$

[0035]The basis of the numbers 247-252, 259-264, 271-276, 319-324, 331-336 which have a methacrylate group in the meso gene group of these polymerization nature is a basis of the numbers 259-264 desirable still more preferably. As for these meso gene groups, what was combined with the straight chain or the annular polysiloxane system main chain is preferred from the good characteristic being shown, and what was combined with the annular polysiloxane is still more preferred.

[0036]As a synthesizing method of these liquid crystal oligomers, the method of a description is employable as JP,S63-47759,B or JP,H2-149544,A. For example, the method of polymerizing the acrylic ester which has the method of making the meso gene group of this side chain adding to a polysiloxane chain, and a meso gene group, via the spacer group of flexibility, and methacrylic acid ester is illustrated. In adding a meso gene group to a polysiloxane chain, It is obtained by making the reaction raw materials which have the same

structure as the meso gene group of the side chain of repeating unit (I) or (II), and have omega-alkenyloxy group which has an unsaturated double bond at the end which generates the alkyleneoxy group which is a spacer react to a polysiloxane under a platinum catalyst. To this reaction time, the rate of a binding fraction of two kinds of meso gene groups is controllable by the reaction-raw-materials preparation ratio corresponding to a non-polymerizable meso gene group and the meso gene group of polymerization nature. When similarly carrying out copolymerization of two kinds of monomers which have a meso gene group with which a main chain corresponds by the acrylic ester system or alpha-alkyl acrylic ester system, the ratio of a polymerization nature meso gene group and a non-polymerizable meso gene group can be controlled by controlling the preparation ratio of a monomer. Thus, that the obtained liquid crystal oligomer indicates a nematic phase or a smectic phase to be used preferably. This liquid crystal oligomer may be used independently, and two or more sorts may be mixed and used for it. The liquid crystal oligomer and low-molecular-liquid-crystal compound which consist only of repeating unit (I) may be mixed and used. However, the content to which mechanical intensity is not substantially reduced in this case is preferred, and 50 or less % of the weight is illustrated. It is 30 or less % of the weight still more preferably. The value at 30 \*\* of the retardation (R) which is the refractive index anisotropy (deltan) of a phase difference film and the product of film thickness (d) containing the polymer of a liquid crystal oligomer, It is not less than 100 nm, is not less than 200 nm 3000 nm or less preferably, and is the not less than 300-nm range of 1500 nm or less still more preferably. Since the temperature dependence of letter DESHON of this phase difference film also needs to follow in footsteps of temperature dependence of a liquid crystal cell, The values of ratio [ of the value ( $R_{80}$ ) at 80 \*\* to the R value ( $R_{30}$ ) at 30 \*\* ], i.e.,  $R_{80}/R_{30}$  are 0.95-0.5, and are 0.9-0.7 preferably.

[0037]The member used for below by this invention is explained in order. As for the polymer of the liquid crystal oligomer of the phase difference film of this invention, using with a thin film is preferred, and it is usually formed on a substrate. As a substrate used at this time, inorganic substrates, such as glass, and a high polymer film or the phase difference film which consists of a thermoplastic polymer which has a positive peculiar double reflex is used. Inorganic compounds, Ceramics Sub-Division, etc., such as oxides, such as the outside of a glass plate transparent as an inorganic substrate or translucent or the glass plate used for a liquid crystal cell, Si, aluminum, Mg, Zr, and fluoride, are illustrated.

[0038]As a high polymer film, polycarbonate, polysulfone, polyarylate, Polyether sulphone, diacetic acid cellulose, cellulose triacetate, polystyrene, An ethylene vinyl alcohol copolymer, polyethylene terephthalate, polyethylenenaphthalate, etc. are illustrated, and polycarbonate, polysulfone, cellulose triacetate, polyethylene terephthalate, and polystyrene are illustrated preferably.

[0039]In the manufacturing method of the phase difference film of this invention, heat-treat in order to arrange the optical axis of a liquid crystal oligomer in a film plane, but. The substrate with which change of an optical property or shape does not take place with heat treatment temperature is preferred, and Polymer Division with high flow temperature is mentioned with a polymer material with thermoplastic engineering Polymer Division with a high glass transition temperature, or Polymer Division in which the plasticizer is added. Although the glass transition temperature of Polymer Division does not have restriction in particular, not less than 100 \*\* is not less than 110 \*\* still more preferably preferably. Cellulose triacetate, polycarbonate, polysulfone, polyether sulphone, and polyethylene terephthalate are preferred as Polymer Division which fulfills this condition.

[0040]As thickness of the high polymer film used for these substrates, 1 micrometers or more 500 micrometers or less of not less than 10 micrometers 300 micrometers or less are not less than 40 micrometers 200 micrometers or less especially preferably desirable still more preferably.

[0041]What is necessary is just to use forming processes, such as the solvent cast method, an extrusion method, the calendar molding method, and a press-forming method, as a manufacturing method of these high polymer films.

[0042]In order to form a liquid crystal oligomer on a high polymer film, it is also possible to dissolve in a solvent and to apply this liquid crystal oligomer so that it may mention later, but in order to give solvent resistance to a high polymer film in the case of spreading, a publicly known solvent resistance film may be formed in the surface. How to vapor-deposit inorganic compounds, such as oxides, such as Si, aluminum, Mg, and Zr, and fluoride, on the surface as a formation method of a solvent resistance film concretely; A polyvinyl alcohol polyethylene vinyl alcohol copolymer, Method; or the polyurethane system which applies water-soluble Polymer Division of pullulan, dextrin, etc., After applying monomers, such as an acrylic oligomer system, an acrylic silicon system, or organopolysiloxane system resin, the method of constructing a bridge in three dimensions in between monomers in thermal polymerization or photopolymerization, etc. are illustrated.

[0043]The wettability of these surface treatment films and solvents of a liquid crystal oligomer is bad, and when there is a problem in the membranous quality of a coating film, the surface treatment technique may be given to a surface treatment film, and may be reformed and used for it. The method of processing with plasma, such as oxygen, as reforming, the way wavelength irradiates with ultraviolet rays of 300 nm or less, and the method of carrying out corona treatment are illustrated.

[0044]Inorganic substrates and the high polymer films mentioned above, such as glass which the value at 30 \*\* of the retardation in this invention described above as a substrate of 100 nm or less, and Ceramics Sub-Division, can be used. The cellulose triacetate, polycarbonate, polysulfone, or polyether sulphone which is immediately after membrane formation and is not extended by the film especially as a high polymer film is preferred. Although the smaller one of the retardation of these substrates it can consider that are isotropic optically is preferred, since it is technically difficult also from a viewpoint of a manufacturing cost to use 0 nm, a substrate of 100 nm or less is preferred, and a substrate of 70 nm or less can use it conveniently more preferably.

[0045]In transferring the phase difference film containing the polymer of a liquid crystal oligomer, The substrate which uses a liquid crystal oligomer for membrane formation and orientation does not need to be transparent or translucent, and it is also possible to use metal as a substrate which has an orientation means on the surface in addition to inorganic substrates, such as the above-mentioned glass and Ceramics Sub-Division. What processed into belt shape boards and these metal, such as aluminum which ground the surface as metal, and stainless steel, is illustrated.

[0046]Next, as thermoplastic Polymer Division which has a positive peculiar double reflex used the substrate of the phase difference film containing the polymer of a liquid crystal oligomer, or when laminating, Polycarbonate, polysulfone, polyarylate, polyether sulphone, diacetic acid cellulose, cellulose triacetate, polyvinyl alcohol, a polyethylene vinyl alcohol copolymer, polyethylene terephthalate, etc. are mentioned. Uniaxial orientation of this thermoplastic polymer is extended and carried out, and it uses as a phase difference film. The phase difference film which consists of these thermoplastic polymers may be used as a substrate of a liquid crystal oligomer, and with a liquid crystal oligomer, it may paste together or laminate and it may be used.

[0047]What is necessary is just to use forming processes, such as the solvent cast method, an extrusion method, and a press-forming method, as a manufacturing method of a film (it may be hereafter called a raw fabric film.) used as a raw material of the phase difference film which consists of these thermoplastic polymers. As an extension method which uses this raw fabric film as the phase difference film which has an optical axis in a film plane, and which carried out uniaxial orientation, the tenter extending method, a roll slowing growth method,

the roll compression extending method, etc. are illustrated. In order to obtain a homogeneous phase difference film, it is preferred to extend the film which formed membranes by the solvent cast method by the tenter extending method or a roll slowing growth method.

[0048]As for the viewpoint of productivity to obtaining a uniform phase difference film and thickness, although what is necessary is just to choose the thickness of a phase difference film suitably according to the temperature variation amount of the retardation of the liquid crystal oligomer and phase difference film which are mentioned later, 50-200 micrometers is preferred.

[0049]Next, the method of using an orienting film as an orientation means used by this invention, and the method of carrying out rubbing of the surface of a substrate directly not using an orienting film are illustrated. If level orientation of the liquid crystal oligomer is carried out as an orienting film, it is usable in a publicly known thing. For example, inorganic substances, such as hydrophilic giant molecules, such as what carried out photo-curing of the photo-setting resins, such as thermosetting resin, such as polyimide and polyamide, and acrylic oligomer, and polyvinyl alcohol, silica, and alumina, are illustrated. After forming the thin film of such materials on a substrate, level orientation of the polymerization nature liquid crystal oligomer can be carried out by carrying out rubbing. As another kind of an orienting film, the diagonal vapor deposition method film which carried out the diagonal vapor deposition method of the inorganic compounds, such as oxides, such as Si, aluminum, Mg, and Zr, and fluoride, etc. is also illustrated.

[0050]About the thickness of an orienting film, if it is generally 0.01 or more micrometers, orientation performance will be demonstrated, but if an orienting film is too thick, since workability will worsen, 0.01 to 5.0 micrometer is 0.02 to 3.0 micrometer desirable still more preferably. Since solvent resistance will be lost if too thin when using the surface treatment film for giving solvent resistance as an orienting film, 0.1 to 10.0 micrometer is desirable still more preferred, and the thickness of the orienting film in this case is 0.5 to 5.0 micrometer.

[0051]The surface treatment film for improvement in the solvent resistance of a high polymer film mentioned above may be used as an orienting film. For example, in the case of a water-soluble poly membrane, when an inorganic compound is vapor-deposited on the surface, after carrying out a diagonal vapor deposition method or hardening in the case of thermosetting resin or a photo-setting resin, after water evaporates, rubbing of the resin layer may be carried out. Although it already said that a surface treatment method may be used for the wettable improvement in the liquid crystal oligomer dissolved in the surface treatment film and the solvent, it is more desirable from a viewpoint of the stacking tendency of a liquid crystal oligomer to perform it, before such surface treatment carries out rubbing of the surface treatment film.

[0052]Next, the manufacturing method of the phase difference film which consists of liquid crystal oligomer polymer which has an optical axis is described taking the case of the case where a liquid crystal oligomer is formed on a substrate, in the film plane of this invention.

[0053]An orienting film is produced to up to the first above-mentioned substrate. The publicly known method according to an orienting film can be used for the method of producing the orienting film to a substrate top. In the case of the orienting film of an inorganic substance, it is preferred to perform membrane formation with a oblique vapor deposition method. The method of using the jig which specifically inclines a substrate at a suitable angle to a deposition source, and the method of forming membranes using the method of forming a baffle between an evaporation source and a substrate and changing the direction of an emission, by resistance heating vacuum deposition, electron beam heating vacuum deposition, or sputtering process are mentioned. Electron beam heating vacuum deposition and sputtering process are preferred also in these.

[0054]In the case of the orienting film of resin, rubbing is performed after applying on a substrate. When using a high polymer film as a substrate, the homogeneity of an orienting

film from an improving viewpoint. Processing which enlarges surface tension of these high polymer films by publicly known surface treatment art, such as processing using plasma treatment, corona treatment, UV irradiation, acid, or alkali of the surface of a high polymer film or the high polymer film which was mentioned above, and which carried out the surface treatment, may be performed. As a method of applying an orienting film, the roll coat method, the gravure coating method, the bar coat method, a spin coat method, a spray coating method, the printing method, the DEPPINGU method, etc. are illustrated. Since uniform thickness with sufficient productivity is obtained also in this, the roll coat method, the gravure coating method, and the bar coat method are preferred.

[0055]It heat-treats, when using thermosetting resin as an orienting film. Heat treatment temperature can be suitably chosen in consideration of the softening temperature and productivity of a substrate which are used. When using a photo-setting resin as an orienting film, publicly known curing methods, such as ultraviolet curing, are used. Rubbing is performed by grinding the orienting film surface against a buff cloth or a hair transplantation roller. There is no restriction in particular about the pressure applied to the kinds and these rubbing material of cloth or a roller. When using glass, Ceramics Sub-Division, and metal as a substrate, the above-mentioned orienting film may be provided on these substrates, and rubbing of these base material surfaces may be carried out directly. The construction material used for rubbing may use the buff cloth mentioned above, the cloth into which suspension other than a hair transplantation roller, such as a sandpaper of more than No. 1000 and alumina with fine particle diameter, was infiltrated, etc.

[0056]Subsequently, a liquid crystal oligomer is formed on the substrate which has an orienting film. The method which the method of applying by solution states and the method of applying by an isotropic phase state are illustrated, and applies a liquid crystal oligomer from solution states as a method for film deposition of a liquid crystal oligomer is preferred. As a coating method, the usual roll coat method, the gravure coating method, the bar coat method, a spin coat method, a spray coating method, the printing method, the DEPPINGU method, etc. are illustrated. Since uniform thickness with sufficient productivity is obtained also in this, the roll coat method, the gravure coating method, and the bar coat method are preferred.

[0057]As thickness of a liquid crystal oligomer film, 0.1-20 micrometers is 0.5-10 micrometers desirable still more preferably, and it is 1-7 micrometers especially preferably. Since it will be hard to carry out orientation if the grade of a manifestation of the optical characteristic will become small if thinner than 0.1 micrometer, and it exceeds 20 micrometers, it is not desirable.

[0058]Subsequently, a liquid crystal oligomer is heat-treated. If heat treatment temperature is beyond the temperature a liquid crystal oligomer indicates a liquid crystal phase to be, there will be no restriction in particular, but. If heat treatment temperature is low close to a glass phase or crystal phase transition temperature, orientation takes time and it is not desirable from an industrial viewpoint, Since the problem of changing [ which are a substrate and an orienting film ] will arise if heat treatment temperature is high, it elapses and the glass transition temperature or add-in material of a substrate to be used becomes in the substrate added more than the flow temperature of a substrate, it is not desirable. When the liquid crystal phase / isotropic phase transition temperature of a liquid crystal oligomer will be written to be Ti and the temperature which modification of a substrate and an orienting film produces will be written to be Ts, \*\* - (Ts-30) \*\* are \*\*(Ti-50) -(Ts-40) \*\* desirable still more preferably as heat treatment temperature (Ti-60). About the heating rate in heat treatment, and a cooling rate, since it is industrially disadvantageous if temperature up and a cooling rate are small, the larger one is preferred, the above is specifically preferred by 10 \*\*/, and the above is still more preferred by 100 \*\*/. Although there is no restriction in particular also about heat treating time, if not much short, a stacking tendency is not enough, since it is not industrially desirable if not much long, 20 or less hours is preferred 0.2 minute or more,

and 1 or less hour is still more preferred 1 minute or more. By the above heat treatment, orientation of the meso gene group of a liquid crystal oligomer is carried out within a film plane, and it comes to have an optical axis in a film plane.

[0059]After carrying out orientation treatment so that it may have an optical axis in a film plane, a polymerization nature liquid crystal oligomer is polymerized. Since to polymerize holding orientation as a polymerization method is required, radiation initiated polymerization, such as photopolymerization and a gamma ray, and thermal polymerization are illustrated. A publicly known polymerization initiator can be used in photopolymerization or thermal polymerization. Simplicity to photopolymerization and thermal polymerization of a process are preferred in these polymerization methods, and photopolymerization is still more preferred from good [ of maintenance of orientation ].

[0060]If there is too little light volume, maintenance of orientation is not perfect, if there is too much light volume, since productivity will worsen, the irradiation light quantity of the light used for photopolymerization has preferred 50 - 10000 mJ/cm<sup>2</sup>, and its 100 - 5000 mJ/cm<sup>2</sup> is more preferably preferred.

[0061]In the manufacturing method of the phase difference film of this invention, a liquid crystal oligomer is formed on a film on the substrate (it is hereafter called the substrate A.) which has an orientation means, and after heat-treating and polymerizing, it is also possible to exfoliate from a substrate and to transfer to other substrates (it is hereafter called the substrate B.). As for transfer of the liquid crystal oligomer from the substrate A to the substrate B, it is preferred to use a binder, The method of laminating the substrate B with a binder on the substrate A with a liquid crystal oligomer film, and exfoliating a liquid crystal oligomer film from the substrate A, After removing the separator of one side of the binder of the person-not-qualified-as-a-senior-official type with which the binder was pinched by the separator (substrate of a mold-release characteristic) of two sheets, it laminates in the substrate A (or the substrate B), After laminating the separator of one side which remains in the peel-off substrate B (or the substrate A), the method of exfoliating a liquid crystal oligomer film from the substrate A (or the substrate B) is illustrated.

[0062]The temperature change rates of the retardation of the phase difference film which has the phase difference film or liquid crystal oligomer polymer which consists of liquid crystal oligomer polymer of this invention, and a substrate, Since it is possible to choose suitably the repeating unit and spacer length of a liquid crystal oligomer, it can choose so that it may become the optimal according to the temperature change rates of the STN cell used in combination. Namely, what is necessary is to also enlarge the temperature change rates of a phase difference film according to it, when the temperature change rates of a STN cell are large, and just to also make small the temperature change rates of a phase difference film according to it, when the temperature change rates of a STN cell are small. In order to enlarge the temperature change of the retardation of the phase difference film which consists of liquid crystal oligomer polymer, the method of making small the number of repeating units of a liquid crystal oligomer, or lengthening the spacer length which connects a meso gene to a main chain, and lowering the viscosity of this liquid crystal oligomer is illustrated. The method of making low the degree of cross linking of a polymerization nature liquid crystal oligomer is also effective. On the contrary, in order to make small the temperature change of the retardation of the phase difference film which consists of liquid crystal oligomer polymer, the method of enlarging the number of repeating units of a liquid crystal oligomer, or making brief the spacer length which connects a meso gene to a main chain, and raising the viscosity of this liquid crystal oligomer is illustrated. The method of making high the degree of cross linking of a polymerization nature liquid crystal oligomer is illustrated.

[0063]The phase difference film which has liquid crystal oligomer polymer using the phase difference film which becomes a substrate from a thermoplastic polymer which is another gestalt of this invention, and a substrate, In order to enlarge the temperature change of the

retardation of this phase difference film in the case of the phase difference film which pasted together or laminated the phase difference film which consists of liquid crystal oligomer polymer, and the phase difference film which consists of thermoplastic polymers, Thickness of the phase difference film which consists of thermoplastic polymers in addition to the method mentioned above is made small, and the method of enlarging thickness of a liquid crystal oligomer phase difference film, the method of enlarging draw magnification of the phase difference film which consists of thermoplastic polymers, etc. are illustrated. In order to make small the temperature change of the retardation of this phase difference film, a method contrary to the method mentioned above is illustrated.

[0064]In the liquid crystal display of this invention, if the position which arranges the phase difference film which consists of liquid crystal oligomer polymer, and the phase difference film which has liquid crystal oligomer polymer and a substrate is between the polarizing plate of a liquid crystal display, and a liquid crystal cell, there will be no restriction in particular.

[0065]

[Example]Hereafter, although working example explains this invention in detail, this invention is not limited to this. The glass transition point of the obtained liquid crystal oligomer and the transition temperature of a liquid crystal phase and an isotropic phase were evaluated with observation by polarizing microscope and a differential scanning calorimeter (DSC). The liquid crystal oligomer was scanned by a part for scan speed/of 10 \*\*, and transition temperature was evaluated from the data of the 2nd henceforth. Under [ all / Ti / endothermic peak / which is considered to consider about Tg that the peak of the primary differential of the endothermic curve at the time of temperature up is Tg, and to be based on a liquid crystal phase / isotropic phase transition about Ti ].

[0066]The retardation of the phase difference film was measured by the double reflex measuring method of SENARUMON using the polarization microscope which equipped the SENARUMON compensator. A measured wavelength is 546 nm.

[0067]After having dissolved working example 1 poly AMIKU acid in N-methyl pyrrolidone, considering it as the solution 3% and carrying out a spin coat on a glass plate, it heat-treated at 200 \*\* for every substrate for 3 hours, and the polyimide film of 0.02 micrometer thickness was obtained. Rubbing of the polyimide film furthermore obtained was carried out with the nylon hair transplantation roller. It is made to be the same as that of a method given in JP,S63-41400,B, 4 -(allyl-oxy)- Benzoic acid-4'-cyanophenyl ester and 4 -(allyloxy)- Benzoic acid-(4'-meta-clo yloxy phenyl) ester is made to react to pentamethyl cyclopentasiloxane with the mixture ratio of 1:1, The annular pentasiloxane liquid crystal oligomer which has a non-polymerizable meso gene group and a polymerization nature meso gene group was obtained. This liquid crystal oligomer checked structure from ultimate analysis, the infrared absorption spectrum, and the <sup>1</sup>H-NMR spectrum.

[0068]Tg of the obtained polymerization nature liquid crystal oligomer was 18.7 \*\*, and Ti was 117.5 \*\*. This polymerization nature liquid crystal oligomer was dissolved so that it might become 20wt% in toluene, and further, as photopolymerization start material, trade name IRGACURE 907 (made by Ciba-Geigy) was mixed so that it might become 2wt% to a liquid crystal oligomer. On the glass substrate which attached the polyimide orientation film which carried out rubbing, the spin coat method was used and this polymerization nature liquid crystal oligomer solution was applied. The obtained glass / polyimide / liquid crystal oligomer (it means that / is laminated.) were heated for 1 minute on the hot plate heated at 150 \*\*, and it cooled.

[0069]It quenches, when the obtained polymerization nature liquid crystal oligomer film is placed so that a rubbing direction may become parallel to the absorption axis of a polarizing plate under cross Nicol, Since the retardation was shown when the rubbing direction had been arranged in the direction which is not parallel to the absorption axis of a polarizing plate, it turned out that level orientation of the polymerization nature liquid crystal oligomer is carried

out. It glared so that addition irradiation light quantity might become 1000 mJ/cm<sup>2</sup> on the polymerization nature liquid crystal oligomer film which was able to acquire the ultraviolet rays of the high-pressure mercury lamp. When the temperature change of the retardation of the obtained liquid crystal oligomer polymer film was measured, it came to be shown in drawing 1 and it turned out that the temperature change of a retardation is reversible within the limits of an error of measurement. The arrow in a figure shows the order of a temperature change (it is the same hereafter.).

[0070]Liquid crystal oligomer polymer film is laminated so that front contrast may become the maximum on the STN panel. Even if it heats the obtained STN display at 60 \*\*, a black and white display becomes possible.

[0071]The polymerization nature liquid crystal oligomer film was obtained like working example 1 except not irradiating with comparative example 1 ultraviolet rays. Although level orientation of the obtained polymerization nature liquid crystal oligomer film was carried out, the temperature change of the retardation came to be shown in drawing 2, and was not reversible.

[0072]It is a phase difference film made from polycarbonate as a phase difference film which has an optical axis in comparative example 2 film plane, and has a positive peculiar double reflex, which consists of thermoplastic polymers and which carried out uniaxial orientation. [Trade name SUMIKARA Ito (SEF-400426) Sumitomo Chemical Co., Ltd. make, When the temperature dependence of the retardation with a retardation 380nm and an angle of visibility of 39 degrees] was measured, the rate of the temperature change of a retardation was smaller than the phase difference film which consists of liquid crystal oligomer polymer which showed change as shown in drawing 3, and was indicated in working example 1.

[0073]After carrying out the spin coat of the working example 2 light cross-linking hard court agent [trade name Sumi FREX XR-11:Sumitomo Chemical Co., Ltd. make] on a glass substrate, it irradiated with the ultraviolet rays of high-pressure-water silver and a lamp so that addition irradiation light quantity might become 1000 mJ/cm<sup>2</sup>, and the hard court film was obtained. Oxygen plasma treatment of the obtained glass substrate with a hard court film was carried out (50 mW is impressed on pressure 0. 05Torr and 13.56 MHz RF frequency). The substrate which performs rubbing like working example 1 after plasma treatment, and has an orienting film was obtained. It heat-treated by having formed the liquid crystal oligomer like working example 1 on the obtained substrate, and irradiated with ultraviolet rays, and the phase difference film was obtained. Since it quenched when it had arranged so that the obtained phase difference film may show a 133.6-nm retardation and a rubbing direction may become parallel to the absorption axis of a polarizing plate under cross Nicol, it turned out that level orientation of the polymerization nature liquid crystal oligomer is carried out.

[0074]After carrying out rubbing of the glass substrate with a comparative example 3 hard-court film, the polymerization nature liquid crystal oligomer film was obtained like working example 2 except having carried out plasma treatment. Although the obtained polymerization nature liquid crystal oligomer film was placed under cross Nicol and it rotated in the level surface, it quenched in the omnidirection. Next, since the retardation appeared when it inclined around arbitrary axes, it turned out that perpendicular orientation of the polymerization nature liquid crystal oligomer is carried out.

[0075]Polyvinyl alcohol was used as an orienting film instead of polyimide of working example 3 working example 1, and glass / polyvinyl alcohol / polymerization nature liquid crystal oligomer was obtained like working example 1 except having heat-treated for 3 minutes at 130 \*\*. It turned out that the obtained polymerization nature liquid crystal oligomer film shows a 208.5-nm retardation, and level orientation is carried out from there being an extinction position under cross Nicol. The obtained polymerization nature liquid crystal oligomer film was irradiated with the ultraviolet rays from a high-pressure mercury lamp so that it might become 1000 mJ/cm<sup>2</sup> with addition light volume. After sticking a binder

on a liquid crystal oligomer film and pasting together with a triacetic acid cellulose film, polyvinyl alcohol is melted by underwater [ which was heated at 60 \*\* ], and a liquid crystal oligomer film is transferred to a triacetic acid cellulose film. Measurement of the retardation of the obtained cellulose triacetate / binder / liquid crystal oligomer will show a reversible temperature change.

[0076]The polymerization nature liquid crystal oligomer film which carries out level orientation like working example 3 is obtained except using metal belts, such as a polyethylene terephthalate (PET) film and stainless steel, as a substrate instead of the glass plate of working example 4 working example 3, Thermoplastic polymers which have an isotropic film and positive peculiar double reflex optically, such as a triacetic acid cell roll, are transferred on the phase difference film etc. which carried out uniaxial orientation. The retardation of the obtained cellulose triacetate / binder / liquid crystal oligomer shows a reversible temperature change.

[0077]

[Effect of the Invention]Since the phase difference film of this invention can obtain a phase difference film with the temperature dependence of a retardation near a STN cell, it can fit temperature change rates easily according to the temperature change rates of the liquid crystal display cell used in combination. The manufacturing method of the phase difference film of this invention has unnecessary heat treatment in an elevated temperature, and it is industrially advantageous. The liquid crystal display using the phase difference film of this invention can raise the display properties in an elevated temperature remarkably.

## TECHNICAL FIELD

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[Industrial Application]This invention relates to the liquid crystal display using the phase difference film used for a super twist nematic (it may be hereafter called STN.) mold liquid crystal display element etc., its manufacturing method, and this phase difference film.

## PRIOR ART

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[Description of the Prior Art]As a light and thin planar display, the liquid crystal display is used for the indicator of a personal computer or a various device. The field used with a distribution cost is also expanded with improvement in the characteristic. The environment used also spreads in connection with it, and to operate at an elevated temperature or low temperature is demanded. As a liquid crystal display, the STN type thing is widely used for the display of a word processor or a personal computer. In the present STN type liquid crystal display, the birefringence of a liquid crystal layer is compensated with a phase difference film (generally called color compensation), and what realized black and white or a colored presentation is used. Although using the liquid crystal layer for compensation for phase contrast compensation was performed in early stages, the high polymer film which carried out uniaxial orientation is generally used now. However, there is expansion of the use field also by a STN type liquid crystal display element, and the environment which uses an element has spread. The request of improvement of the new characteristic has come out in connection with it. One of them is that change of the quality of a display to a temperature change is small. For example, by a car, a temperature in the car changes with seasons a lot. In this case, there was a problem to which each retardations (optical phase contrast) of a liquid crystal cell and a phase difference film differ at an elevated temperature or low temperature, and display properties worsen.

[0003]That is, if temperature becomes high, a retardation will become small with relaxation of the orientation of a liquid crystal element or Polymer Division, but generally the orientation

relaxation of the low-molecular liquid crystal currently used for the liquid crystal cell is larger, and change of a retardation also has it. [ larger than orientation relaxation of Polymer Division currently used for the phase difference film ] For this reason, both retardation currently optimized at the room temperature shifts from an optimal condition at an elevated temperature, color compensation of a liquid crystal cell becomes imperfect, problems, like coloring arises arise, and display properties fall. Thus, the phase difference film using a high polymer film was not necessarily ideal for characteristic improvement of a liquid crystal cell, when removing the viewpoint of color compensation. For this reason, the trial which uses a liquid crystal material for a phase difference film is also reported.

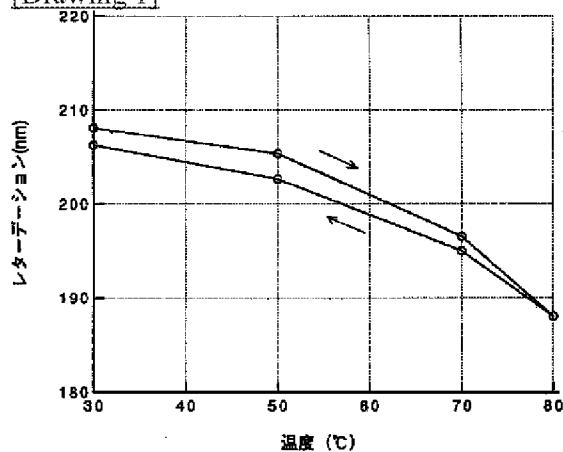
[0004]The solution which dissolved liquid crystallinity Polymer Division which becomes JP,H3-291601,A from the polyester which includes an orthosubstitution aromatic unit substantially is applied on the substrate which has a publicly known orienting film, As for more than the glass transition temperature of liquid crystallinity Polymer Division, by heat-treating below with liquid crystal phase-isotropic phase transition temperature, carry out level orientation, it is made to cool below to glass transition temperature, and what fixed orientation is illustrated. In this, the liquid crystallinity polymer material beyond the temperature which glass transition temperature uses is illustrated. The side chain type liquid crystal polymer and elastomer which have a straight chain or an annular main chain are used for JP,H4-500284,A, After extending a film above the glass transition temperature over 50 \*\*, or impressing a magnetic field and an electric field above a glass transition point and carrying out orientation of the meso gene group, it is indicated that fix orientation below with glass transition temperature, and a phase difference film is obtained. The siloxane chain which has glass transition temperature in the temperature region desirable in WO 92/No. 14180 gazette and higher than the maximum of service temperature beyond a room temperature in it, Uniaxial orientation of the liquid crystal polymer which makes a skeleton an acrylic chain or a meta-acrylic chain is heated and carried out, and the optically anisotropic body obtained by the method of quenching is indicated.

[0005]However, orientation of the meso gene group of a polymer liquid crystal needed to be carried out under heating, it needed to be cooled below to glass transition temperature, and orientation needed to be made to fix in the phase difference film using the Polymer Division liquid crystal material indicated until now. The polymer material which has a glass transition temperature higher than service temperature needed to be used. Since the glass transition point is higher than a room temperature, in order to carry out orientation of the optical axis of a liquid crystal polymer into a field, an elevated temperature needs to be heat-treated. In the temperature range to be used, since a polymer liquid crystal is a vitreous state, it has a problem to which the temperature dependence of a double refraction factor does not often necessarily follow in footsteps of the temperature change of the retardation of a liquid crystal cell unlike a liquid crystal cell. It had a fault, such as it being difficult to obtain material with a low glass transition temperature, for example, phase difference films with a mechanical strength enough in a liquid crystal oligomer, on the other hand, and it being difficult to deal with it industrially, and being. Thus, the phase difference film in which near temperature dependence is shown by the temperature dependence of the retardation of the liquid crystal cell for a display was called for.

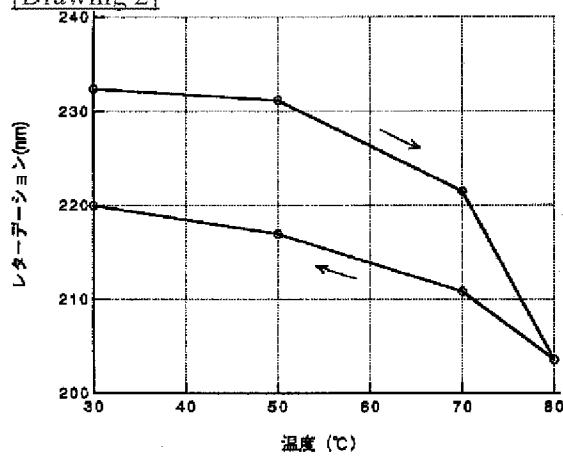
## DRAWINGS

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[Drawing 1]



[Drawing 2]



[Drawing 3]

